CBSE Class 12 Chemistry (Set 56/5/1) Question Paper with Solutions

Time Allowed :3 Hour	**Maximum Marks :**70	**Total Questions :**33

General Instructions

Read the following instructions very carefully and strictly follow them:

- Answers to this Paper must be written on the paper provided separately.
- You will not be allowed to write during the first 15 minutes
- This time is to be spent in reading the question paper.
- The time given at the head of this Paper is the time allowed for writing the answers,
- The paper has four Sections.
- Section A is compulsory - All questions in Section A must be answered.
- You must attempt one question from each of the Sections B, C and D and one other question from any Section of your choice.

1. Which of the reactions is used in the conversion of a ketone into hydrocarbon?
(A) Reimer-Tiemann reaction
(B) Wolff-Kishner reduction
(C) Aldol condensation
(D) Stephen reaction

Correct Answer: (B) Wolff-Kishner reduction

Solution: Concept: To convert a ketone into a hydrocarbon, the carbonyl group ($C = O$) must be completely removed and replaced by hydrogen atoms. This type of transformation is called **reduction of carbonyl compounds to alkanes**. Two major reactions do this:

- Clemmensen reduction (acidic medium)
- Wolff-Kishner reduction (basic medium)

Among the given options, only one performs complete reduction of a ketone to a hydrocarbon.
Step 1: Understanding each option.
(A) Reimer-Tiemann reaction: Used for formylation of phenols to give salicylaldehyde. It does **not reduce ketones**.
(B) Wolff-Kishner reduction: This reaction converts aldehydes or ketones into hydrocarbons using hydrazine (NH_2NH_2) and strong base at high temperature:

$$R{-}CO{-}R' \xrightarrow[\text{KOH, heat}]{NH_2NH_2} R{-}CH_2{-}R'$$

Thus, the carbonyl group is completely removed.

(C) Aldol condensation: Forms β-hydroxy aldehydes/ketones or α, β-unsaturated compounds. It is a **C–C bond forming reaction**, not a reduction.
(D) Stephen reaction: Used to convert nitriles into aldehydes. It is unrelated to ketone reduction.
Step 2: Final selection. Only the Wolff-Kishner reduction converts a ketone into a hydrocarbon.

$$\therefore \text{Correct answer} = \text{(B) Wolff-Kishner reduction}$$

Quick Tip

Remember: - **Clemmensen reduction** → Acidic conditions (Zn-Hg/HCl) - **Wolff-Kishner reduction** → Basic conditions (Hydrazine + KOH)
Both convert carbonyl groups into hydrocarbons.

---

2. Which of the following reagents are used to prepare primary amines by Hofmann bromamide degradation reaction?

(i) $R-\overset{\overset{O}{\|}}{C}-NH_2$ (ii) NaOH

(iii) Br_2 (iv) $CHCl_3$

(A) (i), (ii) and (iv)
(B) (i) and (iii)
(C) (i), (ii) and (iii)
(D) (i), (iii) and (iv)

Correct Answer: (C) (i), (ii) and (iii)

Solution: Concept: The **Hofmann bromamide degradation reaction** (also called Hofmann rearrangement) is used to convert a primary amide into a primary amine with **one carbon less**. The reaction involves rearrangement and loss of the carbonyl carbon as CO_2.
General reaction:

$$R–CONH_2 \xrightarrow{Br_2/NaOH} R–NH_2 + CO_2$$

Thus, the essential reagents are:

- Primary amide ($R–CONH_2$)
- Bromine (Br_2)
- Strong base (NaOH or KOH)

Step 1: Analyze each given option.
(i) $R–CONH_2$**:** This is the starting compound (primary amide). ⇒ Required.
(ii) NaOH: Provides the basic medium needed for rearrangement and formation of hypobromite intermediate. ⇒ Required.

(iii) Br_2**:** Essential reagent that forms sodium hypobromite ($NaOBr$) in situ. ⇒ Required.
(iv) CHCl$_3$: Used in the carbylamine reaction (test for primary amines), not in Hofmann rearrangement. ⇒ Not required.
Step 2: Final selection. Correct set of reagents:

$$(i), (ii), (iii)$$

$$\therefore \text{Correct answer} = \text{(C)}$$

Quick Tip

Hofmann Rearrangement Shortcut: Amide → Amine with **one carbon less**.
Reagents to remember:

$$Br_2 + NaOH \quad \text{(basic bromine)}$$

---

3. The major product of carbylamine reaction is:
(A) Carboxylic acid
(B) Aldehyde
(C) Cyanide
(D) Isocyanide

Correct Answer: (D) Isocyanide

Solution: Concept: The **carbylamine reaction** is a characteristic test for primary amines. When a primary amine is heated with chloroform ($CHCl_3$) and alcoholic KOH, it forms a foul-smelling compound called an **isocyanide (carbylamine)**.
General reaction:

$$R{-}NH_2 + CHCl_3 + 3KOH \rightarrow R{-}NC + 3KCl + 3H_2O$$

Step 1: Reaction insight. Primary amines react with chloroform in the presence of base to produce:

$$R{-}NC \quad \text{(isocyanide)}$$

Step 2: Eliminate incorrect options.

- Carboxylic acid — not formed in this reaction.
- Aldehyde — unrelated transformation.
- Cyanide ($R{-}CN$) — different functional group from isocyanide.

Step 3: Final answer.

$$\therefore \text{Major product} = \text{Isocyanide}$$

Quick Tip

Carbylamine test detects **primary amines only**. Product formed: **Isocyanide (foul smell)**.

4. Actinoids show larger number of oxidation states:
(A) because they are electropositive in nature
(B) because they have large atomic numbers
(C) because they have large atomic size
(D) due to comparable energies of 5f, 6d and 7s orbitals

Correct Answer: (D) due to comparable energies of 5f, 6d and 7s orbitals

Solution: Concept: Actinoids exhibit a wide range of oxidation states due to the involvement of multiple orbitals in bonding. Unlike lanthanoids, actinoids have:

- Partially filled 5f orbitals
- Accessible 6d orbitals
- Outer 7s electrons

Because the energies of these orbitals are very close, electrons from all three can participate in bonding.
Step 1: Analyze the reason. When orbitals of similar energy levels are available, multiple electrons can be lost or shared, leading to variable oxidation states.
Step 2: Evaluate options.

- Electropositivity — not the main reason.
- Large atomic number — not directly related to oxidation states.
- Large atomic size — minor factor.
- Comparable energies of 5f, 6d, 7s orbitals — correct reason.

Step 3: Conclusion.

$$\therefore \text{Correct answer} = \text{(D)}$$

Quick Tip

Key Difference: Lanthanoids → mostly +3 oxidation state Actinoids → variable oxidation states due to participation of 5f, 6d, and 7s orbitals.

---

5. Consider the following reaction and identify A and B:

$$CH_3Cl + NaI \xrightarrow{\text{dry acetone}} A + B$$

(A) A = CH_3I, B = NaCl
(B) A = CH_3OH, B = NaCl
(C) A = CH_3CHO, B = NaCl
(D) A = C_2H_6, B = CH_3I

Correct Answer: (A) A = CH_3I, B = NaCl

Solution: Concept: This reaction represents the **Finkelstein reaction**, which involves halogen exchange in alkyl halides. It is an S_N2 reaction where a chlorine atom is replaced by iodine using sodium iodide in dry acetone.
General reaction:

$$R\text{–}Cl + NaI \xrightarrow{\text{acetone}} R\text{–}I + NaCl$$

The reaction proceeds forward because $NaCl$ is insoluble in acetone and precipitates out, driving the reaction to completion.
Step 1: Identify the reaction type. Presence of NaI in dry acetone strongly indicates Finkelstein reaction.
Step 2: Apply halogen exchange.

$$CH_3Cl + NaI \rightarrow CH_3I + NaCl$$

Step 3: Identify products.

- A = CH_3I (methyl iodide)
- B = NaCl (precipitate)

$$\therefore \text{Correct answer} = \text{(A)}$$

Quick Tip

Finkelstein Reaction Shortcut:

$$R\text{–}Cl/Br + NaI \xrightarrow{\text{acetone}} R\text{–}I$$

Driven by precipitation of NaCl or NaBr.

---

6. The correct formula of Hinsberg's reagent is:
(A) C_6H_5COCl
(B) $C_6H_5SO_2Cl$
(C) $C_6H_5CONHCH_3$
(D) $C_6H_6CH_2NH_2$

Correct Answer: (B) $C_6H_5SO_2Cl$

Solution: Concept: Hinsberg's reagent is used in the **Hinsberg test** to distinguish between primary, secondary, and tertiary amines. The reagent used is **benzenesulphonyl chloride**.
Formula:

$$C_6H_5SO_2Cl$$

Step 1: Recall the Hinsberg test.

- Primary amines → soluble sulphonamide (in alkali)
- Secondary amines → insoluble sulphonamide

- Tertiary amines → no reaction

Step 2: Identify correct formula.

- C_6H_5COCl → Benzoyl chloride (incorrect)
- $C_6H_5SO_2Cl$ → Benzenesulphonyl chloride (correct)
- Others are unrelated compounds

$$\therefore \text{Correct answer} = \text{(B)}$$

Quick Tip

Hinsberg Reagent = Benzenesulphonyl chloride Formula to remember: $C_6H_5SO_2Cl$

---

7. Half-life ($t_{1/2}$) of a first order reaction is 1386 s. The value of rate constant is:
(A) $0.5 \times 10^{-4}\,\text{s}^{-1}$
(B) $5.0 \times 10^{-4}\,\text{s}^{-1}$
(C) $0.5 \times 10^{-5}\,\text{s}^{-1}$
(D) $0.5 \times 10^{-3}\,\text{s}^{-1}$

Correct Answer: (A) $0.5 \times 10^{-4}\,\text{s}^{-1}$

Solution: Concept: For a **first order reaction**, the half-life is independent of initial concentration and is given by:

$$t_{1/2} = \frac{0.693}{k}$$

where k is the rate constant.
Step 1: Use the half-life formula. Given:

$$t_{1/2} = 1386\,\text{s}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386}$$

Step 2: Simplify the value. Note that:

$$1386 = 0.693 \times 2000$$

Hence,

$$k = \frac{0.693}{0.693 \times 2000} = \frac{1}{2000}$$

Step 3: Convert to scientific notation.

$$k = \frac{1}{2000} = 5 \times 10^{-4} \div 10 = 0.5 \times 10^{-4}\,\text{s}^{-1}$$

Step 4: Match with options.

$$\therefore \text{Correct answer} = \text{(A)}$$

Quick Tip

For first order reactions:

$$t_{1/2} = \frac{0.693}{k}$$

If half-life is known, rate constant can be found directly without concentration data.

8. Which of the following ligands forms a chelate complex?
(A) Ammonia
(B) Water
(C) NO_2
(D) Oxalate ion

Correct Answer: (D) Oxalate ion

Solution: Concept: A **chelate complex** is formed when a ligand attaches to a metal ion through **two or more donor atoms**, creating a ring structure. Such ligands are called **polydentate ligands**.

Step 1: Understand ligand types.

- Monodentate ligand → one donor atom
- Bidentate ligand → two donor atoms (forms chelate)

Step 2: Analyze the given ligands.
(A) Ammonia (NH_3): Monodentate ligand → binds through nitrogen only.
(B) Water (H_2O): Monodentate ligand → binds through oxygen.
(C) NO_2: Usually acts as ambidentate but not chelating in typical coordination.
(D) Oxalate ion ($C_2O_4^{2-}$): Bidentate ligand with two oxygen donor atoms. Forms a ring with the metal → chelation.
Step 3: Conclusion.

$$\therefore \text{Chelating ligand} = \text{Oxalate ion}$$

Quick Tip

Common chelating ligands: Oxalate ($C_2O_4^{2-}$), Ethylenediamine (en), EDTA. They form stable ring complexes (Chelate effect).

9. Primary, secondary and tertiary alcohols can be distinguished by:
(A) Lucas test
(B) Fehling's test
(C) Tollens' test
(D) Hinsberg's test

Correct Answer: (A) Lucas test

Solution: Concept: The **Lucas test** is used to distinguish between primary, secondary, and tertiary alcohols based on their reactivity with Lucas reagent (conc. HCl + anhydrous $ZnCl_2$). Reaction: Alcohol → Alkyl chloride (insoluble, turbidity appears)

Step 1: Basis of differentiation. The rate of formation of turbidity differs:

- Tertiary alcohol → Immediate turbidity
- Secondary alcohol → Turbidity in few minutes
- Primary alcohol → No turbidity at room temperature

Step 2: Eliminate incorrect options.

- Fehling's test → For aldehydes
- Tollens' test → For aldehydes
- Hinsberg's test → For amines

Step 3: Final answer.

$$\therefore \text{Correct answer} = \text{Lucas test}$$

Quick Tip

Lucas Test Memory Trick: 3° alcohol → Instant cloudiness 2° alcohol → Slow cloudiness 1° alcohol → No cloudiness (cold conditions)

---

10. Consider the following compounds:

$$(C_2H_5)_2NH, \quad C_6H_5NH_2, \quad C_6H_5CH_2NH_2, \quad NH_3, \quad (C_2H_5)_3N$$

The correct increasing order of the above bases on the basis of their basic strength is:

(A) $C_6H_5NH_2$ ¡ NH_3 ¡ $C_6H_5CH_2NH_2$ ¡ $(C_2H_5)_3N$ ¡ $(C_2H_5)_2NH$
(B) NH_3 ¡ $C_6H_5NH_2$ ¡ $C_6H_5CH_2NH_2$ ¡ $(C_2H_5)_3N$ ¡ $(C_2H_5)_2NH$
(C) $C_6H_5NH_2$ ¡ $(C_2H_5)_2NH$ ¡ NH_3 ¡ $C_6H_5CH_2NH_2$ ¡ $(C_2H_5)_3N$
(D) $C_6H_5NH_2$ ¡ $C_6H_5CH_2NH_2$ ¡ NH_3 ¡ $(C_2H_5)_2NH$ ¡ $(C_2H_5)_3N$

Correct Answer: (A)

Solution:
Concept: Basic strength of amines depends upon the availability of the lone pair of electrons on nitrogen for protonation. The more easily nitrogen donates its lone pair, the stronger the base.
Factors affecting basic strength:

- **+I effect (electron donating effect)** of alkyl groups increases basicity.
- **Resonance effect** decreases basicity by delocalizing the lone pair.
- **Solvation effect** stabilizes protonated species in aqueous solution.

- **Steric hindrance** reduces effective protonation in tertiary amines.

Step 1: Analyze each compound.
(i) $C_6H_5NH_2$ (Aniline): The lone pair on nitrogen is delocalized into the benzene ring due to resonance.

$$\text{Lone pair participates in resonance} \Rightarrow \text{Less available for protonation}$$

Hence, it is the weakest base among the given compounds.
(ii) NH_3: No alkyl group, no resonance. Moderate basic strength.
(iii) $C_6H_5CH_2NH_2$ (Benzylamine): The benzene ring is not directly attached to nitrogen; hence no resonance effect on lone pair. The –CH_2 group exerts +I effect. Therefore, stronger base than ammonia.
(iv) $(C_2H_5)_3N$ (Tertiary amine): Strong +I effect from three alkyl groups increases electron density on nitrogen. However, steric hindrance and poor solvation slightly reduce its strength compared to secondary amine.
(v) $(C_2H_5)_2NH$ (Secondary amine): Strong +I effect and better solvation compared to tertiary amine. Generally strongest base in aqueous solution.
Step 2: Arrange in increasing order of basic strength.

$$\text{Aniline} < NH_3 < \text{Benzylamine} < \text{Tertiary amine} < \text{Secondary amine}$$

$$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

$$\therefore \text{Correct answer} = \text{(A)}$$

Quick Tip

In aqueous solution:

$$\text{Secondary amine} > \text{Tertiary amine} > \text{Primary amine} > NH_3$$

Aniline is least basic due to resonance.

---

11. Identify the polysaccharide among the following:
(A) Fructose
(B) Maltose
(C) Glucose
(D) Cellulose

Correct Answer: (D) Cellulose

Solution:
Concept: Carbohydrates are classified based on the number of monosaccharide units:

- **Monosaccharides** – Single sugar unit (e.g., glucose, fructose)
- **Disaccharides** – Two sugar units (e.g., maltose)

- **Polysaccharides** – Large number of monosaccharide units (e.g., starch, cellulose)

Step 1: Analyze each option.
(A) Fructose: Monosaccharide (simple sugar).
(B) Maltose: Disaccharide composed of two glucose units.
(C) Glucose: Monosaccharide.
(D) Cellulose: Polymer of β-D-glucose units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds. It is a structural polysaccharide found in plant cell walls.
Step 2: Conclusion.

$$\therefore \text{Polysaccharide} = \text{Cellulose}$$

Quick Tip

Examples of polysaccharides: Starch, Glycogen, Cellulose. All are polymers of glucose.

---

12. The polypeptide chain in a protein has amino acids linked with each other in a specific sequence. This specific sequence of amino acids is called:
(A) Primary structure of protein
(B) Secondary structure of protein
(C) Tertiary structure of protein
(D) Quaternary structure of protein

Correct Answer: (A) Primary structure of protein

Solution:
Concept: Proteins have four levels of structural organization:

- **Primary structure** – Linear sequence of amino acids.
- **Secondary structure** – Local folding (-helix, -pleated sheet).
- **Tertiary structure** – Overall 3D folding of a single polypeptide.
- **Quaternary structure** – Association of multiple polypeptide chains.

Step 1: Understand the question. The question refers to the **specific order** in which amino acids are linked.
Step 2: Identify correct structural level. The linear arrangement of amino acids connected by peptide bonds defines the **primary structure**.

$$\text{Amino acid}_1 - \text{Amino acid}_2 - \text{Amino acid}_3 - \dots$$

Step 3: Eliminate other options.

- Secondary → hydrogen bonding patterns.
- Tertiary → 3D folding.
- Quaternary → multiple subunits.

$$\therefore \text{Correct answer} = \text{(A)}$$

Quick Tip

Primary structure = **Sequence**. If sequence changes → protein function may change.

---

13. Assertion (A): D(+)-Glucose is dextrorotatory in nature.
Reason (R): (+) represents dextrorotatory nature and D represents its configuration.
(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of Assertion (A).
(C) Assertion (A) is true, but Reason (R) is false.
(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A)

Solution:
Concept: In carbohydrate chemistry, the symbols **D/L** and **(+)/(−)** have different meanings:

- **D/L notation** → Refers to the **configuration** of the molecule relative to glyceraldehyde.
- **(+)/(−) notation** → Refers to the **optical rotation** of plane-polarized light.

Step 1: Analyze Assertion (A). D(+)-Glucose means:

- D → Configuration similar to D-glyceraldehyde
- (+) → Rotates plane-polarized light to the right (dextrorotatory)

Hence, it is dextrorotatory. ⇒ Assertion is true.
Step 2: Analyze Reason (R). The reason states:

- (+) represents dextrorotation → Correct
- D represents configuration → Correct

This directly explains why D(+)-glucose is dextrorotatory.
Step 3: Logical connection. Since the reason correctly explains the assertion:

$$\therefore \text{Both A and R are true and R explains A}$$

Quick Tip

Important Distinction: D/L → Configuration (structure) (+)/(–) → Optical activity (experimentally observed)
D does NOT always mean dextrorotatory.

---

14. Assertion (A): Highest oxidation state of Mn is +7 in most of the transition elements.
Reason (R): Transition metals exhibit variable oxidation states.
(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of Assertion (A).
(C) Assertion (A) is true, but Reason (R) is false.
(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (D)

Solution:
Step 1: Analyze Assertion (A). Manganese exhibits a maximum oxidation state of +7 (e.g., in $KMnO_4$). However, the statement says "in most of the transition elements," which is incorrect because many transition elements do not reach +7 oxidation state. $\Rightarrow$ Assertion is false.
Step 2: Analyze Reason (R). Transition metals show variable oxidation states due to participation of both ns and $(n-1)d$ electrons in bonding. $\Rightarrow$ Reason is true.

$$\therefore \text{Assertion is false but Reason is true}$$

Quick Tip

Mn shows maximum +7 oxidation state, but not all transition metals do. Variable oxidation state is a general property of transition elements.

---

15. Assertion (A): p-nitrophenol is more acidic than phenol.
Reason (R): Nitro group is an electron-withdrawing group; it stabilizes phenoxide ion by dispersal of negative charge.
(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of Assertion (A).
(C) Assertion (A) is true, but Reason (R) is false.
(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A)

Solution:
Step 1: Analyze Assertion (A). p-Nitrophenol contains a nitro group ($-NO_2$) at the para position. This increases acidity compared to phenol. $\Rightarrow$ Assertion is true.
Step 2: Analyze Reason (R). The nitro group is strongly electron-withdrawing due to:

- $-I$ effect (inductive)

- $-R$ effect (resonance)

It stabilizes the phenoxide ion by delocalizing negative charge over the nitro group.
Step 3: Logical connection. The increased stability of conjugate base directly increases acidity.

$$\therefore \text{Both A and R are true and R explains A}$$

Quick Tip

Electron-withdrawing groups increase phenol acidity. Order: Nitro phenol ¿ Phenol ¿ Alkyl phenol

---

16. Assertion (A): All aliphatic aldehydes give a positive Fehling's test.
Reason (R): Aliphatic aldehydes are reduced by Fehling's reagent.
(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of Assertion (A).
(C) Assertion (A) is true, but Reason (R) is false.
(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (C)

Solution:
Step 1: Analyze Assertion (A). Aliphatic aldehydes generally give a positive Fehling's test by reducing cupric ions to cuprous oxide (red precipitate). ⇒ Assertion is true.
Step 2: Analyze Reason (R). The reason states aldehydes are reduced by Fehling's reagent. This is incorrect — actually, aldehydes **reduce** Fehling's reagent and are themselves oxidized to carboxylic acids.

$$R\text{–}CHO \rightarrow R\text{–}COOH$$

⇒ Reason is false.

$$\therefore \text{Assertion true, Reason false}$$

Quick Tip

Fehling's Test: Aldehyde = reducing agent → oxidized to acid $Cu^{2+} \rightarrow Cu_2O$ (red precipitate)

---

17 (a). 1.00 molal aqueous solution of trichloroacetic acid is heated to its boiling point. The boiling point of this solution was found to be 100.18°C. Calculate the Van't Hoff factor for trichloroacetic acid. (Given: K_b for water = 0.512 K kg mol^{-1})

Solution:
Concept: Elevation in boiling point is a colligative property and is given by:

$$\Delta T_b = i\,K_b\,m$$

where:

- i = Van't Hoff factor
- K_b = ebullioscopic constant
- m = molality

Step 1: Calculate elevation in boiling point.

$$\Delta T_b = 100.18 - 100 = 0.18\,\mathrm{K}$$

Step 2: Substitute values into formula.

$$0.18 = i \times 0.512 \times 1$$

Step 3: Solve for Van't Hoff factor.

$$i = \frac{0.18}{0.512} \approx 0.35$$

Step 4: Interpretation. A value less than 1 indicates association of solute molecules in solution (dimerization or higher aggregation).

$$\therefore i \approx 0.35$$

Quick Tip

If $i < 1 \rightarrow$ Association of molecules If $i > 1 \rightarrow$ Dissociation into ions

---

17 (b). State Henry's law. Calculate the mole fraction of CO_2 in water at 298 K under 700 mm Hg pressure. (Given: Henry's constant for CO_2 in water at 298 K = 1.25×10^6 mm Hg)

Solution:
Henry's Law: At constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

$$p = K_H\,x$$

where:

- p = partial pressure of gas
- K_H = Henry's constant
- x = mole fraction of gas in solution

Step 1: Write the formula.

$$x = \frac{p}{K_H}$$

Step 2: Substitute given values.

$$x = \frac{700}{1.25 \times 10^6}$$

Step 3: Simplify.

$$x = \frac{7 \times 10^2}{1.25 \times 10^6} = \frac{7}{1.25} \times 10^{-4}$$

$$x = 5.6 \times 10^{-4}$$

Final Answer:

$$\therefore \text{Mole fraction of CO}_2 = 5.6 \times 10^{-4}$$

Quick Tip

Henry's Law Shortcut: Higher Henry constant → Lower solubility of gas.

---

18. (a) Name the cell which was used in the Apollo space programme for providing electrical power.

Solution:

Concept: Space missions require a continuous and reliable source of electrical energy. In the Apollo space programme, electrical energy was produced using electrochemical cells that convert chemical energy directly into electrical energy.

Step 1: Identify the type of cell. The Apollo spacecraft used the **Hydrogen–Oxygen fuel cell**.

Step 2: Working principle. In this fuel cell:

- Hydrogen is oxidized at the anode.
- Oxygen is reduced at the cathode.
- The overall reaction produces water and releases electrical energy.

Overall reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Step 3: Advantage in space missions.

- High efficiency
- Continuous power supply
- Water formed was used by astronauts

$\therefore$ The cell used was Hydrogen–Oxygen fuel cell.

Quick Tip

Fuel cells convert chemical energy directly into electrical energy. Apollo missions used H_2–O_2 fuel cells.

(b) Define limiting molar conductivity.

Solution:

Concept: Molar conductivity (Λ_m) increases with dilution because interionic interactions decrease. At infinite dilution, ions move independently and conductivity reaches its maximum value.

Definition: Limiting molar conductivity (Λ_m°) is defined as the molar conductivity of an electrolyte at infinite dilution, where each ion contributes independently to the total conductivity.

Mathematically:

$$\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$$

where:

- λ_+° = limiting molar conductivity of cation
- λ_-° = limiting molar conductivity of anion

Explanation: At infinite dilution:

- Interionic attraction becomes negligible.
- Ions attain maximum mobility.
- Conductivity depends only on individual ionic contributions.

$\therefore$ Λ_m° represents maximum molar conductivity of an electrolyte.

Quick Tip

At infinite dilution: Interionic forces → Zero Conductivity → Maximum $\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$

---

19. (a) Complete the following equation:

Solution:

Concept: This is an example of an **azo coupling reaction**. Aromatic diazonium salts react with activated aromatic compounds like phenol or aniline to form azo compounds ($-N = N-$).
Step 1: Reaction type. Benzenediazonium chloride reacts with phenol in alkaline medium.
Step 2: Role of alkaline medium. In basic solution:

- Phenol forms phenoxide ion.
- Phenoxide is strongly activated toward electrophilic substitution.

Step 3: Position of coupling. Coupling occurs mainly at the **para position** relative to the –OH group due to less steric hindrance.
Step 4: Product formed. The product is **p-hydroxyazobenzene** (an azo dye).

$$C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{OH^-} p\text{-Hydroxyazobenzene} + HCl$$

Final Answer:

p-Hydroxyazobenzene (Azo dye)

Quick Tip

Azo coupling: Diazonium salt + Activated aromatic ring → Azo dye ($-N = N-$).

(b) How will you convert nitromethane to methyl isocyanide?

Solution:
Concept: Nitroalkanes can be reduced to primary amines, and primary amines can be converted into isocyanides via the **carbylamine reaction**.
Step 1: Reduction of nitromethane to methylamine. Nitromethane is reduced using reducing agents such as:

- H_2/Ni
- Sn/HCl
- Fe/HCl

$$CH_3NO_2 \xrightarrow{[H]} CH_3NH_2$$

Step 2: Convert methylamine to methyl isocyanide. Use carbylamine reaction:

$$CH_3NH_2 + CHCl_3 + 3KOH \rightarrow CH_3NC + 3KCl + 3H_2O$$

Step 3: Overall conversion.

$$CH_3NO_2 \xrightarrow{Reduction} CH_3NH_2 \xrightarrow[\text{KOH}]{CHCl_3} CH_3NC$$

Final Answer: Nitromethane → Methylamine (reduction) → Methyl isocyanide (carbylamine reaction).

Quick Tip

Conversion trick: Nitro → Amine (Reduction) Primary amine + $CHCl_3$/KOH → Isocyanide

---

20. (a) What are the products obtained on hydrolysis of sucrose?

Solution:
Concept: Sucrose is a disaccharide composed of two monosaccharide units:

- Glucose
- Fructose

These are linked through a glycosidic bond between:

$$\alpha\text{-D-glucose and }\beta\text{-D-fructose}$$

Step 1: Hydrolysis of sucrose. When sucrose is hydrolysed using:

- Dilute acid (HCl or H_2SO_4)
- Enzyme invertase (sucrase)

the glycosidic bond breaks.
Step 2: Products formed.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

These two monosaccharides are:

- D-glucose
- D-fructose

Step 3: Additional note. The mixture formed is called **invert sugar** because optical rotation changes from dextrorotatory to levorotatory.

$$\therefore \text{Hydrolysis products} = \text{Glucose and Fructose}$$

Quick Tip

Sucrose hydrolysis gives: Glucose + Fructose = Invert sugar

(b) What are essential amino acids?

Solution:
Concept: Amino acids are the building blocks of proteins. Based on the body's ability to synthesize them, they are classified into:

- Essential amino acids
- Non-essential amino acids

Definition: Essential amino acids are those amino acids which cannot be synthesized by the human body in sufficient amounts and must be obtained through diet.
Explanation: Since the body cannot produce them, they must be supplied by protein-rich foods such as:

- Milk
- Eggs
- Meat
- Pulses and legumes

Examples of essential amino acids:

- Valine
- Leucine
- Isoleucine
- Lysine
- Methionine
- Threonine
- Phenylalanine
- Tryptophan

Importance:

- Required for growth and repair of tissues
- Essential for enzyme and hormone synthesis
- Important for immune function

$$\therefore \text{Essential amino acids must be supplied through diet.}$$

Quick Tip

Essential amino acids = Not synthesized in body → Must be taken in food.

---

21. (a) Write any two fat soluble vitamins.

Solution:
Concept: Vitamins are classified based on their solubility into:

- Fat-soluble vitamins
- Water-soluble vitamins

Fat-soluble vitamins: These vitamins dissolve in fats and oils and are stored in body tissues (especially liver and adipose tissue).
Examples:

- Vitamin A
- Vitamin D
- Vitamin E
- Vitamin K

Answer: Any two fat-soluble vitamins:

$$\text{Vitamin A and Vitamin D}$$

Quick Tip

Fat-soluble vitamins: A, D, E, K (remember: ADEK).

(b) How will you confirm the presence of five –OH groups in a glucose molecule, which are attached to different carbon atoms?

Solution:
Concept: Glucose contains multiple hydroxyl ($-OH$) groups. The presence and number of these groups can be confirmed through acetylation reactions.
Step 1: Acetylation of glucose. When glucose is treated with:

- Acetic anhydride ($(CH_3CO)_2O$)
- In presence of pyridine

all hydroxyl groups get acetylated.
Step 2: Formation of glucose pentaacetate.

$$\text{Glucose} + 5(CH_3CO)_2O \rightarrow \text{Glucose pentaacetate} + 5CH_3COOH$$

Step 3: Interpretation. Formation of **pentaacetate** confirms:

- Presence of five hydroxyl groups
- Each attached to a different carbon atom

Conclusion: Since glucose forms a pentaacetate derivative, it confirms that glucose contains five alcoholic $-OH$ groups.

$$\therefore \text{Glucose has five hydroxyl groups.}$$

Quick Tip

Glucose + Acetic anhydride → Glucose pentaacetate Confirms 5 –OH groups.

---

22. Calculate emf of the following cell at 298 K:

$$\mathrm{Cr(s)}\,|\,\mathrm{Cr}^{3+}(aq)\,(0.1\,M)\,||\,\mathrm{Fe}^{2+}(aq)\,(0.01\,M)\,|\,\mathrm{Fe(s)}$$

Given:

$$E^\circ_{\mathrm{Cr}^{3+}/\mathrm{Cr}} = -0.74\,V, \quad E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.44\,V, \quad \log 10 = 1$$

Solution:
Concept: The emf of a galvanic cell under non-standard conditions is calculated using the **Nernst equation**:

$$E = E^\circ - \frac{0.0591}{n}\log Q \quad \text{(at 298 K)}$$

Where:

- E° = standard cell potential
- n = number of electrons transferred
- Q = reaction quotient

Step 1: Identify anode and cathode. Higher reduction potential → cathode.

$$E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.44V > -0.74V$$

So:

- Cathode: $\mathrm{Fe}^{2+}/\mathrm{Fe}$
- Anode: $\mathrm{Cr}/\mathrm{Cr}^{3+}$

Step 2: Write half reactions.
Anode (oxidation):

$$\mathrm{Cr} \rightarrow \mathrm{Cr}^{3+} + 3e^-$$

Cathode (reduction):

$$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe}$$

Step 3: Balance electrons. LCM of 3 and 2 = 6 electrons.
Multiply:

$$2(\mathrm{Cr} \rightarrow \mathrm{Cr}^{3+} + 3e^-)$$

$$3(\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe})$$

Overall reaction:

$$2\mathrm{Cr} + 3\mathrm{Fe}^{2+} \rightarrow 2\mathrm{Cr}^{3+} + 3\mathrm{Fe}$$

Thus, $n = 6$

Step 4: Calculate standard emf.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ = (-0.44) - (-0.74) = +0.30\,V$$

Step 5: Calculate reaction quotient Q.

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

Substitute concentrations:

$$Q = \frac{(0.1)^2}{(0.01)^3}$$

Convert to powers of 10:

$$0.1 = 10^{-1}, \quad 0.01 = 10^{-2}$$

$$Q = \frac{(10^{-1})^2}{(10^{-2})^3} = \frac{10^{-2}}{10^{-6}} = 10^4$$

Step 6: Apply Nernst equation.

$$E = 0.30 - \frac{0.0591}{6}\log(10^4)$$

Since $\log 10^4 = 4$:

$$E = 0.30 - \frac{0.0591 \times 4}{6}$$

$$E = 0.30 - \frac{0.2364}{6}$$

$$E = 0.30 - 0.0394$$

$$E \approx 0.26\,V$$

Final Answer:

$$\therefore \text{Cell emf} \approx 0.26\,V$$

Quick Tip

Steps for emf problems: 1. Identify anode and cathode 2. Balance electrons → find n 3. Calculate Q 4. Apply Nernst equation

---

23. (a) Define order of a reaction.

Solution:

Concept: In chemical kinetics, the rate of a reaction depends on the concentration of reactants. This dependence is expressed through the rate law.

For a general reaction:

$$aA + bB \rightarrow \text{Products}$$

Rate law:

$$\text{Rate} = k[A]^m[B]^n$$

Definition: The **order of a reaction** is defined as the sum of the powers of the concentration terms appearing in the rate law.
Mathematically:

$$\text{Order} = m + n$$

Types of order:

- Zero order → Rate independent of concentration
- First order → Rate depends on one reactant
- Second order → Sum of powers = 2
- Fractional order → Non-integer values possible

Important Note: Order is determined experimentally and may not match stoichiometric coefficients.

$$\therefore \text{Order} = \text{Sum of powers of concentration terms in rate law.}$$

Quick Tip

Order stoichiometric coefficient. It is determined experimentally from rate law.

(b) The rate for the following reaction is given by:

$$A + B \rightarrow C, \quad \text{Rate} = k[A][B]^2$$

(i) How is the rate affected if we double the concentration of B?

Solution:
Given:

$$\text{Rate} = k[A][B]^2$$

If concentration of B is doubled:

$$[B] \rightarrow 2[B]$$

New rate:

$$\text{Rate}' = k[A](2[B])^2 = k[A] \cdot 4[B]^2$$

$$\text{Rate}' = 4 \times \text{original rate}$$

Answer: Rate becomes four times.

Quick Tip

If rate $[\mathrm{B}]^2$, doubling B increases rate by 4× (square dependence rule).

(ii) Write the overall order of a reaction if A is present in large excess.

Solution:

Concept: If one reactant is present in large excess, its concentration remains nearly constant during the reaction. The reaction then behaves as a **pseudo-order reaction**.

Given rate law:

$$\text{Rate} = k[A][B]^2$$

If A is in large excess:

$$[A] = \text{constant}$$

Let:

$$k' = k[A]$$

Then rate becomes:

$$\text{Rate} = k'[B]^2$$

Effective order: Now rate depends only on $[B]^2$.

$$\therefore \text{Overall order} = 2 \text{ (pseudo second order)}$$

Quick Tip

If one reactant is in excess → pseudo-order reaction. Rate depends only on the limiting reactant.

---

24. The rate of a chemical reaction doubles when the temperature is raised from 298 K to 308 K. Calculate the activation energy (E_a) for this reaction assuming it does not change with temperature. (Given: $R = 8.314\,\mathrm{J\ mol^{-1}K^{-1}}$, $\log 2 = 0.30$)

Solution:

Concept: Temperature dependence of reaction rate is given by the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

For two temperatures:

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Step 1: Given data.

$$\frac{k_2}{k_1} = 2 \quad \text{(rate doubles)}$$

$$T_1 = 298\,K, \quad T_2 = 308\,K$$

Step 2: Substitute into Arrhenius form.

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left(\frac{308 - 298}{298 \times 308}\right)$$

Step 3: Simplify temperature term.

$$\frac{T_2 - T_1}{T_1 T_2} = \frac{10}{298 \times 308}$$

$$298 \times 308 = 91784$$

$$\Rightarrow \frac{10}{91784} \approx 1.089 \times 10^{-4}$$

Step 4: Substitute values.

$$0.30 = \frac{E_a}{2.303 \times 8.314} \times 1.089 \times 10^{-4}$$

First calculate denominator:

$$2.303 \times 8.314 \approx 19.15$$

$$0.30 = \frac{E_a}{19.15} \times 1.089 \times 10^{-4}$$

Step 5: Solve for E_a.

$$E_a = \frac{0.30 \times 19.15}{1.089 \times 10^{-4}}$$

$$0.30 \times 19.15 = 5.745$$

$$E_a = \frac{5.745}{1.089 \times 10^{-4}}$$

$$E_a \approx 5.28 \times 10^4 \text{ J mol}^{-1}$$

Step 6: Convert to kJ mol^{-1}.

$$E_a \approx 52.8\,\text{kJ mol}^{-1}$$

Final Answer:

$$\therefore E_a \approx 53\,\text{kJ mol}^{-1}$$

Quick Tip

If rate doubles with 10 K rise → E_a usually 50–60 kJ/mol. Use Arrhenius logarithmic form for temperature change problems.

---

25. (a) Write the IUPAC name of the following complex:

$$K_3[Cr(C_2O_4)_3]$$

Solution:
Step 1: Identify the complex ion. The complex ion is:

$$[Cr(C_2O_4)_3]^{3-}$$

since three K^+ ions balance the charge.
Step 2: Identify ligands. Ligand $C_2O_4^{2-}$ is called **oxalato**. Number of ligands = 3 → prefix = **tris** (used for polydentate ligands).
Step 3: Find oxidation state of Cr. Let oxidation state of Cr = x

$$x + 3(-2) = -3$$
$$x - 6 = -3 \Rightarrow x = +3$$

Step 4: Naming the complex.

- Ligand: tris(oxalato)
- Metal: chromium
- Oxidation state: (III)
- Negative complex → metal name ends with "-ate"

So chromium becomes **chromate**.
Step 5: Add counter ion. Cation present: Potassium
Final Name:

$$\boxed{\text{Potassium tris(oxalato)chromate(III)}}$$

Quick Tip

Negative complex → metal name ends with "-ate". Fe → Ferrate, Cu → Cuprate, Cr → Chromate.

(b) Differentiate between homoleptic complex and heteroleptic complex.

Solution:
Concept: Complexes are classified based on the types of ligands attached to the central metal atom.
Homoleptic Complex:

- Contains only **one type of ligand**.
- All ligands around the metal are identical.
- Example: $[Co(NH_3)_6]^{3+}$

Heteroleptic Complex:

- Contains **more than one type of ligand**.
- Different ligands are coordinated to the metal.

- Example: $[Co(NH_3)_4Cl_2]^+$

Key Difference:

Homoleptic	Heteroleptic
One ligand type Uniform environment	Multiple ligand types Mixed ligand environment

Quick Tip

Homo = Same ligand Hetero = Different ligands

(c) Which type of isomerism is exhibited by the following complex?

$$[Pt(NH_3)_2Cl_2]$$

Solution:
Concept: The complex $[Pt(NH_3)_2Cl_2]$ is a square planar complex of Pt(II). Square planar complexes can show **geometrical isomerism**.
Step 1: Possible arrangements. Two possible arrangements:

- **Cis form** – Similar ligands adjacent to each other.
- **Trans form** – Similar ligands opposite to each other.

Step 2: Types of isomers.

- Cis-$[Pt(NH_3)_2Cl_2]$
- Trans-$[Pt(NH_3)_2Cl_2]$

Conclusion:

$$\therefore \text{The complex exhibits geometrical (cis–trans) isomerism.}$$

Quick Tip

Square planar complexes often show cis–trans isomerism. Classic example: $[Pt(NH_3)_2Cl_2]$ (cisplatin).

---

26. (a) A coordination compound CrCl$_3$·6H_2O is mixed with excess AgNO$_3$ solution, two moles of AgCl are precipitated per mole of the compound. Write the structural formula of the coordination compound.

Solution:
Concept: AgNO$_3$ test is used to determine the number of ionisable chloride ions present outside the coordination sphere.
Step 1: Analyze given data.

- Total chlorides in compound = 3
- 2 moles of AgCl formed → 2 ionisable Cl^-

So:

- 2 Cl^- outside coordination sphere
- 1 Cl^- inside coordination sphere

Step 2: Assign water molecules. Total water molecules = 6 Remaining ligands inside coordination sphere:

$$6 - 0 = 6 \text{ waters available}$$

Chromium(III) typically shows coordination number = 6.
Thus, inner sphere:

$$[Cr(H_2O)_5Cl]^{2+}$$

Step 3: Write full structural formula. Two chloride ions outside:

$$\boxed{[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O}$$

Explanation:

- 1 Cl inside sphere
- 2 Cl outside → gives 2 AgCl
- Remaining 1 water as lattice water

Quick Tip

$AgNO_3$ test → counts free halide ions outside coordination sphere.

(b) Write the oxidation state and hybridisation of the central metal in the following complex:

$$[Fe(H_2O)_6]^{3+} \quad (\text{Atomic number of Fe} = 26)$$

Solution:
Step 1: Find oxidation state of Fe. Water is a neutral ligand.
Let oxidation state of Fe = x

$$x + 6(0) = +3 \Rightarrow x = +3$$

Step 2: Electronic configuration of Fe. Fe (Z = 26):

$$[Ar]\, 3d^6 4s^2$$

Fe^{3+}:

$$3d^5$$

Step 3: Determine hybridisation. Water is a weak field ligand → high spin complex.
For octahedral high spin d^5:

$$\text{Hybridisation} = sp^3d^2$$

Answer:

- Oxidation state = +3
- Hybridisation = sp^3d^2

Quick Tip

Weak field ligands (H_2O, F^-) → high spin → outer orbital complex (sp^3d^2).

(c) Why is $[Ni(H_2O)_6]^{2+}$ coloured? (Atomic number of Ni = 28)

Solution:
Concept: Transition metal complexes are coloured due to **d–d transitions**. These occur when electrons absorb visible light and move between split d-orbitals.
Step 1: Electronic configuration of Ni. Ni (Z = 28):

$$[Ar]\,3d^8 4s^2$$

Ni^{2+}:

$$3d^8$$

Step 2: Effect of ligand field. In octahedral complex:

$$d\text{-orbitals split into } t_{2g} \text{ and } e_g$$

Step 3: Reason for colour.

- Partially filled d-orbitals present
- d–d electronic transitions occur
- Absorption of visible light → complementary colour observed

Conclusion:

$$\therefore [Ni(H_2O)_6]^{2+} \text{ is coloured due to d–d transitions.}$$

Quick Tip

Colour in transition complexes → d–d transitions in partially filled d-orbitals.

---

27. How do you convert the following?
(a) Acetophenone to Benzoic acid

Solution:
Concept: Acetophenone is a methyl ketone. Methyl ketones undergo **haloform reaction** (iodoform reaction) when treated with halogen in alkaline medium, leading to cleavage and formation of carboxylate salt.

Step 1: Haloform reaction.

$$C_6H_5COCH_3 \xrightarrow{I_2/NaOH} C_6H_5COONa + CHI_3$$

Step 2: Acidification.

$$C_6H_5COONa \xrightarrow{H^+} C_6H_5COOH$$

Final Conversion:

$$\text{Acetophenone} \xrightarrow{I_2/NaOH} \text{Sodium benzoate} \xrightarrow{H^+} \text{Benzoic acid}$$

Quick Tip

Methyl ketone + Haloform reaction → Carboxylic acid (one carbon less).

(b) Acetonitrile to Acetone

Solution:

Concept: Nitriles can be converted to ketones using **Grignard reagent** followed by hydrolysis.

Step 1: Reaction with Grignard reagent. Treat acetonitrile with methyl magnesium bromide:

$$CH_3CN + CH_3MgBr \to (CH_3)_2C = NMgBr$$

Step 2: Hydrolysis. On acidic hydrolysis:

$$(CH_3)_2C = NMgBr \xrightarrow{H_3O^+} (CH_3)_2CO$$

Final Conversion:

$$CH_3CN \xrightarrow{CH_3MgBr/H_3O^+} \text{Acetone}$$

Quick Tip

Nitrile + Grignard reagent → Ketone (after hydrolysis).

(c) Benzoic acid to Benzene

Solution:

Concept: Benzoic acid can be converted to benzene by **decarboxylation**. This removes the carboxyl group as CO_2.

Step 1: Soda lime decarboxylation. Heat benzoic acid with soda lime (NaOH + CaO):

$$C_6H_5COONa + NaOH \xrightarrow{CaO,\ \Delta} C_6H_6 + Na_2CO_3$$

Step 2: Formation of sodium salt first.

$$C_6H_5COOH \xrightarrow{NaOH} C_6H_5COONa$$

Final Conversion:

$$\text{Benzoic acid} \xrightarrow{\text{soda lime}} \text{Benzene}$$

Quick Tip

Soda lime decarboxylation removes –COOH as CO_2 → gives hydrocarbon.

---

28. (a) (i) Arrange the following compounds in increasing order of their acidic strengths:

$$CH_3CH_2COOH, \quad CH_3CH(CH_3)COOH, \quad CH_3CH_2CH_2COOH, \quad BrCH_2CH_2COOH$$

Solution:

Concept: Acidity of carboxylic acids depends mainly on:

- Inductive effect of substituents
- Electron-withdrawing groups increase acidity
- Electron-donating alkyl groups decrease acidity

Step 1: Analyze substituent effects.

(1) $CH_3CH(CH_3)COOH$: Branched alkyl group shows strong +I effect → least acidic.

(2) $CH_3CH_2CH_2COOH$: Longer alkyl chain → stronger +I effect than propionic acid → lower acidity.

(3) CH_3CH_2COOH: Moderate +I effect → higher acidity than above two.

(4) $BrCH_2CH_2COOH$: Bromine is electron-withdrawing (I effect) → stabilizes carboxylate ion → most acidic.

Step 2: Arrange in increasing acidity.

$$CH_3CH(CH_3)COOH < CH_3CH_2CH_2COOH < CH_3CH_2COOH < BrCH_2CH_2COOH$$

Quick Tip

I group (like halogen) increases acidity. +I alkyl groups decrease acidity.

(ii) Why is CH_3CHO more reactive than acetone towards reaction with HCN?

Solution:

Concept: Reactivity of carbonyl compounds toward nucleophilic addition depends on:

- Steric hindrance
- +I effect of alkyl groups

Reason 1: Steric factor. Acetaldehyde (CH_3CHO) has one alkyl group, while acetone has two. More crowding in acetone → less reactive.
Reason 2: Inductive effect. Two methyl groups in acetone donate electrons (+I effect), reducing electrophilicity of carbonyl carbon.
Conclusion:

$$\text{CH}_3CHO > \text{Acetone in reactivity toward HCN}$$

Quick Tip

Aldehydes are more reactive than ketones due to less steric hindrance and weaker +I effect.

(iii) Complete the equation:

$$CH_3CHO + NH_2NH_2 \xrightarrow{OH^-} ?$$

Solution:
Concept: This is the **Wolff–Kishner reduction**. Aldehydes or ketones react with hydrazine in basic medium to give alkanes.
Reaction:

$$R–CHO + NH_2NH_2 \xrightarrow{KOH,\ \Delta} R–CH_3 + N_2 + H_2O$$

Apply to acetaldehyde:

$$CH_3CHO \xrightarrow{NH_2NH_2/KOH} CH_3CH_3$$

Product: Ethane

Quick Tip

Wolff–Kishner reduction converts carbonyl group → methylene (CH_2).

(b) An organic compound with molecular formula C_7H_6O forms 2,4-DNP derivative, reduces Tollens' reagent and gives Cannizzaro reaction. On vigorous oxidation it gives benzene-1,2-dicarboxylic acid. Identify the compound. Also write the reactions of the compound with 2,4-DNP and when it undergoes Cannizzaro reaction.

Solution:
Step 1: Interpret given tests.

- Forms 2,4-DNP derivative → Contains carbonyl group

- Reduces Tollens' reagent → Aldehyde
- Undergoes Cannizzaro reaction → Aromatic aldehyde without -H

Step 2: Molecular formula analysis. C_7H_6O suggests benzaldehyde derivatives.
Step 3: Oxidation clue. On vigorous oxidation gives benzene-1,2-dicarboxylic acid (phthalic acid). This implies an ortho-substituted aldehyde.
Hence compound is:

$$\text{o-Hydroxybenzaldehyde (Salicylaldehyde)}$$

Reaction with 2,4-DNP:

$$\text{Aldehyde} + \text{2,4-DNP} \rightarrow \text{Orange precipitate (hydrazone)}$$

$$C_6H_4(OH)CHO + 2,4\text{-DNP} \rightarrow \text{2,4-DNP hydrazone}$$

Cannizzaro Reaction: In presence of strong base:

$$2ArCHO \xrightarrow{NaOH} ArCH_2OH + ArCOONa$$

For salicylaldehyde:

$$2C_6H_4(OH)CHO \xrightarrow{NaOH} C_6H_4(OH)CH_2OH + C_6H_4(OH)COONa$$

Final Answer:

$$\text{Compound} = \text{o-Hydroxybenzaldehyde (Salicylaldehyde)}$$

Quick Tip

Cannizzaro reaction → Aldehydes without -hydrogen. Tollens' positive → Aldehyde confirmed.

---

29. Read the following passage carefully and answer the questions that follow:
Passage:
Ethers are prepared by the dehydration of alcohols in presence of protic acids at 413 K. Symmetrical and unsymmetrical ethers can also be prepared by Williamson synthesis. This reaction involves S_N2 attack of an alkoxide ion on a primary alkyl halide. If tertiary alkyl halide is used, elimination reaction occurs and alkene is formed instead of ether.
C–O bond in ethers are cleaved under drastic conditions with excess of HI. When unsymmetrical ethers react with HI, the alkyl halide is formed from the smaller alkyl group. If one of the alkyl groups is tertiary, the alkyl halide is formed from the tertiary alkyl group because tertiary carbocation is more stable than primary carbocation. Cleavage of alkyl aryl ethers takes place at the alkyl–oxygen bond due to more stable alkyl–oxygen bond.
The order of reactivity of hydrogen halides is:

$$HI > HBr > HCl$$

Aromatic ethers undergo electrophilic substitution reactions. The alkoxy group attached to the aromatic ring activates the ring and directs the incoming group to ortho and para positions.

(a) (i) Complete the following equation:

$$\text{Anisole} + CH_3Cl \xrightarrow{\text{Anhyd. } AlCl_3} ?$$

Solution:

Concept: This is a Friedel–Crafts alkylation reaction. The –OCH$_3$ group activates the benzene ring and directs substitution to ortho and para positions.

Products:

o-Methylanisole and p-Methylanisole (para major)

Quick Tip

–OCH$_3$ group is ortho–para directing and strongly activating.

(a) (ii) Complete the following reaction:

$$\text{Anisole} \xrightarrow{\text{Conc. } HNO_3+H_2SO_4} ?$$

Solution:

Concept: Nitration is an electrophilic substitution reaction. The methoxy group directs nitration to ortho and para positions.

Products:

o-Nitroanisole and p-Nitroanisole (para major)

Quick Tip

Electrophilic substitution in anisole occurs mainly at ortho and para positions.

(b) (i) Write the names of alkyl halide and sodium alkoxide used to prepare tert-butyl ethyl ether by Williamson synthesis.

Solution:

Concept: In Williamson synthesis, primary alkyl halide should be used to avoid elimination. To prepare tert-butyl ethyl ether:

$$(C_2H_5)Cl + (CH_3)_3CONa$$

Answer:

- Alkyl halide: Ethyl chloride
- Sodium alkoxide: Sodium tert-butoxide

Quick Tip

In Williamson synthesis use primary alkyl halide to avoid elimination.

(b) (ii) Anisole on reaction with HI gives phenol and CH_3I and not methanol and iodobenzene. Justify the statement.

Solution:
Concept: Cleavage of alkyl aryl ether occurs at the alkyl–oxygen bond because:

- The aryl–O bond has partial double bond character.
- It is stronger and does not break easily.

$$C_6H_5OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$$

Therefore:

- Phenol is formed.
- Methyl iodide is formed.

Methanol and iodobenzene are not formed because cleavage does not occur at aryl–oxygen bond.

Quick Tip

Alkyl aryl ether cleavage occurs at alkyl–O bond, not aryl–O bond.

(c) Why is C–O–C bond angle in ethers slightly greater than tetrahedral angle?

Solution:
Concept: The tetrahedral bond angle is 109.5°. In ethers:

- Two bulky alkyl groups attached to oxygen repel each other.
- This increases bond angle slightly.

Therefore:

$$\text{C–O–C bond angle} \approx 111^\circ$$

Conclusion: Due to repulsion between bulky alkyl groups, bond angle is slightly greater than 109.5°.

Quick Tip

Greater steric repulsion → Slightly larger bond angle than tetrahedral.

---

30. Read the following passage carefully and answer the questions that follow:

Passage:

Electrochemistry is the study of the relationship between chemical energy and electrical energy. Many spontaneous reactions and corrosion reactions liberate electrical energy. In electrolysis, electrical energy is converted directly into chemical energy. The products of an electrolytic reaction depend on the nature of the material being electrolysed and the type of electrode used. Oxidising and reducing species present in the electrolyte cell and their standard electrode potentials affect the products of electrolysis. Electrolysis plays an important role in most people's daily lives, whether it is for the manufacturing of aluminium, electroplating of metals, or the synthesis of chemical compounds.

Michael Faraday was the first scientist who proposed two laws to explain the quantitative aspects of electrolysis, popularly known as Faraday's laws of electrolysis. Faraday's laws of electrolysis provide a basis for mathematical analysis of the mass deposited at electrodes and the amount of charge passed through them.

Faraday's laws are fundamental in various applications, including electroplating, metal extraction, battery technology and chemical synthesis. These laws also help in environmental monitoring and in various chemistry experiments.

(a) (i) Predict the products of electrolysis in each of the following:

(1) An aqueous solution of $CuCl_2$

Solution:

In aqueous $CuCl_2$:

- Cations: Cu^{2+}, H^+
- Anions: Cl^-, OH^-

At cathode (reduction): Cu^{2+} has higher reduction potential than water.

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

At anode (oxidation): Cl^- is preferentially oxidized.

$$2Cl^- \rightarrow Cl_2(g) + 2e^-$$

Products:

- Cathode: Copper metal
- Anode: Chlorine gas

Quick Tip

In $CuCl_2$ electrolysis: Cu at cathode, Cl_2 at anode.

---

(2) A concentrated solution of H_2SO_4 with platinum electrodes

Solution:

Platinum electrodes are inert.
At cathode: Reduction of H$^+$:

$$2H^+ + 2e^- \rightarrow H_2(g)$$

At anode: Oxidation of water:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Products:

- Cathode: Hydrogen gas
- Anode: Oxygen gas

Quick Tip

Electrolysis of dilute/conc. acids with inert electrodes gives H$_2$ and O$_2$.

(a) (ii) How much charge in Faraday is required for the reduction of 1 mole of Ag$^+$ to Ag?

Solution:
Reduction reaction:

$$Ag^+ + e^- \rightarrow Ag$$

One mole of Ag$^+$ requires 1 mole of electrons.
1 Faraday = charge of 1 mole electrons

$$\therefore \text{Charge required} = 1 \text{ Faraday}$$

Quick Tip

1 mole electrons = 1 Faraday = 96500 C.

OR
(b) (i) State Faraday's second law of electrolysis.

Solution:
Faraday's Second Law: When the same quantity of electricity is passed through different electrolytes, the masses of substances deposited are proportional to their equivalent weights.
Mathematically:

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

Where:

- m = mass deposited

- E = equivalent weight

Quick Tip

Same charge → Mass deposited Equivalent weight.

(ii) The following reactions occur at the anode during electrolysis of aqueous sodium chloride solution:

$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^- \quad E^\circ = 1.36\,V$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^\circ = 1.23\,V$$

Which reaction is feasible at the anode and why?

Solution:
Although oxidation of water has lower potential (1.23 V), in aqueous NaCl:

- Overvoltage for oxygen evolution is high.
- Chloride ions are present in high concentration.

Thus, chloride oxidation occurs preferentially:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Answer: Chlorine evolution is feasible at the anode due to lower overvoltage and high Cl^- concentration.

Quick Tip

In brine electrolysis, Cl_2 forms instead of O_2 due to overvoltage effect.

---

31. (a) (i) Calculate the freezing point of a solution when 10.5 **g of** $MgBr_2$ **was dissolved in 250 g of water, assuming** $MgBr_2$ **undergoes complete dissociation.** (Given: Molar mass of $MgBr_2$ = 184 g mol^{-1}, K_f for water = 1.86 K kg mol^{-1})

Solution:
Concept: Depression in freezing point is given by:

$$\Delta T_f = iK_f m$$

Where:

- i = Van't Hoff factor
- m = molality

Step 1: Calculate moles of solute.

$$\text{Moles of MgBr}_2 = \frac{10.5}{184} = 0.0571\,\text{mol}$$

Step 2: Calculate molality. Mass of water = 250 g = 0.25 kg

$$m = \frac{0.0571}{0.25} = 0.2284\,\text{mol kg}^{-1}$$

Step 3: Van't Hoff factor. MgBr_2 dissociates as:

$$MgBr_2 \to Mg^{2+} + 2Br^-$$

Total ions = 3

$$i = 3$$

Step 4: Calculate depression in freezing point.

$$\Delta T_f = 3 \times 1.86 \times 0.2284$$

$$\Delta T_f = 1.27\,K$$

Step 5: Freezing point of solution.

$$T_f = 0 - 1.27 = -1.27^\circ C$$

Final Answer:

$$\boxed{-1.27^\circ C}$$

Quick Tip

Electrolytes increase depression due to higher Van't Hoff factor.

(a) (ii) Write two differences between ideal and non-ideal solutions.

Solution:
Ideal Solution:

- Obeys Raoult's law at all concentrations.
- No enthalpy change on mixing ($\Delta H_{mix} = 0$).
- No volume change on mixing.

Non-Ideal Solution:

- Deviates from Raoult's law.
- Shows heat change on mixing.
- Volume change occurs.

Two Key Differences:

Ideal	Non-Ideal
Obeys Raoult's law No heat change	Deviates from Raoult's law Heat evolved or absorbed

Quick Tip

Ideal → Similar intermolecular forces. Non-ideal → Different intermolecular forces.

OR (b) (i) A solution is prepared by dissolving 0.088 g of potassium sulphate in 2 L of water at 27°C. Assuming complete dissociation, determine its osmotic pressure. (Given: $R = 0.082\, L\, atm\, K^{-1}\, mol^{-1}$, Molar mass of $K_2SO_4 = 174$ g mol^{-1})

Solution:
Concept: Osmotic pressure:

$$\pi = iCRT$$

Step 1: Moles of solute.

$$\frac{0.088}{174} = 5.06 \times 10^{-4}\, mol$$

Step 2: Molarity. Volume = 2 L

$$C = 2.53 \times 10^{-4}\, M$$

Step 3: Van't Hoff factor.

$$K_2SO_4 \to 2K^+ + SO_4^{2-} \Rightarrow i = 3$$

Step 4: Substitute values.

$$\pi = 3 \times 2.53 \times 10^{-4} \times 0.082 \times 300$$

$$\pi = 0.0187\, atm$$

Final Answer:

$$\boxed{0.019\, atm}$$

Quick Tip

For osmotic pressure always convert temperature to Kelvin.

(b) (ii) What type of azeotrope will be formed by a solution of benzene and chloroform? Give reason.

Solution:
Benzene and chloroform form a **maximum boiling azeotrope**.
Reason:

- Strong intermolecular attraction due to hydrogen bonding between:

$$C_6H_6 \cdots H{-}CCl_3$$

- Negative deviation from Raoult's law.
- Lower vapour pressure → higher boiling point.

Answer: Maximum boiling azeotrope due to strong intermolecular interactions and negative deviation.

Quick Tip

Negative deviation → Maximum boiling azeotrope. Positive deviation → Minimum boiling azeotrope.

---

32. (a) (i) Why do transition metals show variable oxidation states?

Solution:
Transition metals have partially filled $(n-1)d$ orbitals along with outer ns electrons. Both ns and $(n-1)d$ electrons can participate in bonding.
Reason:

- Small energy difference between ns and $(n-1)d$ orbitals
- Electrons from both orbitals are used in bond formation

Hence, different numbers of electrons can be lost.

$$\therefore \text{Transition metals exhibit variable oxidation states.}$$

Quick Tip

Variable oxidation state due to involvement of both ns and (n1)d electrons.

(ii) Out of Mn^{2+} and Zn^{2+}, which ion will be more paramagnetic and why? (Atomic numbers: Mn = 25, Zn = 30)

Solution:
Electronic configurations:
Mn (Z = 25):

$$[Ar]\,3d^5 4s^2 \Rightarrow Mn^{2+} = 3d^5$$

Zn (Z = 30):

$$[Ar]\,3d^{10} 4s^2 \Rightarrow Zn^{2+} = 3d^{10}$$

Magnetic nature:

- Mn^{2+}: 5 unpaired electrons → highly paramagnetic
- Zn^{2+}: No unpaired electrons → diamagnetic

$$\therefore Mn^{2+} \text{ is more paramagnetic.}$$

Quick Tip

More unpaired electrons → Greater paramagnetism.

(iii) Which is the strongest oxidising agent among:

$$Cr^{3+},\ V^{3+},\ Mn^{3+}$$

Solution:
An oxidising agent readily gains electrons (gets reduced).
Among given ions:

- Mn^{3+} easily reduces to Mn^{2+}
- Mn^{2+} has stable half-filled $3d^5$ configuration

Due to stability of half-filled configuration, Mn^{3+} strongly accepts electrons.

$$\therefore Mn^{3+} \text{ is strongest oxidising agent.}$$

Quick Tip

Half-filled and fully filled d-configurations are especially stable.

(iv) Complete and balance the following equations:

(1)

$$2MnO_4^- + 6OH^- \rightarrow ?$$

Solution:
In alkaline medium, permanganate reduces to manganate:

$$2MnO_4^- + 6OH^- \rightarrow 2MnO_4^{2-} + 3H_2O + O_2$$

Quick Tip

In alkaline medium, MnO reduces to MnO² (permanganate → manganate).

(2)

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow ?$$

Solution:
This is a redox reaction in acidic medium:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Quick Tip

Permanganate reductions: Acidic → $\mathrm{Mn^{2+}}$ Neutral → $\mathrm{MnO_2}$ Alkaline → $\mathrm{MnO_4^{2-}}$

OR (b) (i) What is meant by lanthanoid contraction?

Solution:
Lanthanoid contraction refers to the gradual decrease in atomic and ionic radii of lanthanoids with increasing atomic number.
Cause:

- Poor shielding by 4f electrons
- Increased effective nuclear charge

Quick Tip

Lanthanoid contraction affects size and properties of transition elements.

(ii) Why do transition metals form coloured compounds?

Solution:
Transition metal ions have partially filled d-orbitals.

- d-orbitals split in ligand field
- d–d electronic transitions absorb visible light
- Complementary colour observed

$$\therefore \text{Transition metal compounds are coloured.}$$

Quick Tip

Colour arises from d–d transitions in partially filled d-orbitals.

(iii) Why are E° values for Mn and Zn more negative than expected?

Solution:
For Mn:

- Mn^{2+} has stable half-filled $3d^5$ configuration
- Reduction potential becomes more negative

For Zn:

- Zn^{2+} has fully filled $3d^{10}$ configuration
- Greater stability → more negative reduction potential

Quick Tip

Extra stability of half-filled and fully filled orbitals affects E° values.

(iv) Which is the most stable oxidation state of Co and why?

Solution:
Cobalt commonly shows +2 and +3 oxidation states.
Most stable state: +2
Reason:

- Removal of two 4s electrons is easier
- Co^{2+} has relatively stable configuration

Quick Tip

For first-row transition metals, +2 is often most stable oxidation state.

(v) Why is Ce^{4+} in aqueous solution a good oxidising agent?

Solution:
Ce^{4+} easily gets reduced to Ce^{3+}.

- Ce^{3+} has stable configuration
- High tendency to gain electron

Hence, Ce^{4+} acts as a strong oxidising agent.

Quick Tip

Strong oxidising agents readily get reduced to stable lower oxidation states.

---

33. (a) (i) Which of the following is more reactive towards S_N1 reaction: 2-bromo-2-methylbutane or 1-bromopentane?

Solution:
S_N1 reactions proceed via carbocation formation. Stability of carbocation determines reactivity.

- 2-bromo-2-methylbutane → forms tertiary carbocation
- 1-bromopentane → forms primary carbocation

Since tertiary carbocations are more stable:

$$\therefore \text{2-bromo-2-methylbutane is more reactive in } S_N1.$$

Quick Tip

SN1 reactivity: 3° ¿ 2° ¿ 1° due to carbocation stability.

(ii) What type of halide is present in the compound:

$$CH_3 - CH(CH_3) - C(Cl) = CH_2$$

Solution:
The chlorine atom is attached to a carbon involved in a double bond.
Such halides are called **vinylic halides**.

$$\therefore \text{It is a vinylic halide.}$$

Quick Tip

Halogen attached directly to double-bond carbon → Vinylic halide.

(iii) Why is chloroform stored in dark coloured bottles?

Solution:
Chloroform undergoes slow oxidation in presence of light and air to form poisonous phosgene gas ($COCl_2$).

$$CHCl_3 + O_2 \xrightarrow{light} COCl_2 + HCl$$

Dark bottles prevent exposure to light and inhibit this reaction.

Quick Tip

Chloroform stored in dark bottles to prevent formation of toxic phosgene.

(iv) Define the following terms:
(1) Ambident nucleophiles

Solution:
Ambident nucleophiles are nucleophiles that can attack through two different atoms.
Examples:

- CN^- (C or N attack)
- NO_2^-

Quick Tip

Ambident nucleophiles attack via two different atoms (e.g., CN, NO).

(2) Racemic mixture

Solution:
A racemic mixture contains equal amounts of two enantiomers.

- Optically inactive
- Rotations cancel each other

Quick Tip

Racemic mixture = 50:50 mixture of enantiomers → optically inactive.

OR (b) (i) Which isomer of C_4H_9Br is most reactive towards S_N2 reaction?

Solution:
S_N2 reactions are favoured by least steric hindrance.
Among isomers:

- tert-butyl bromide → least reactive
- isobutyl bromide → moderate
- sec-butyl bromide → moderate
- n-butyl bromide → least hindered

∴ n-butyl bromide is most reactive in S_N2.

Quick Tip

SN2 reactivity: Methyl ¿ 1° ¿ 2° ¿¿ 3°.

(ii) Predict the alkene formed by dehydrohalogenation of 1-bromo-1-cyclohexylethane.

Solution:
Dehydrohalogenation follows Saytzeff rule (more substituted alkene preferred).
Removal of HBr forms:

1-ethylcyclohexene (more substituted alkene)

Quick Tip

Elimination reactions usually follow Saytzeff rule → more substituted alkene major.

(iii) Although chlorine shows strong I effect, it is ortho–para directing in electrophilic aromatic substitution. Why?

Solution:
Chlorine has:

- I effect (electron withdrawing)
- +R effect (lone pair donation)

Resonance donation increases electron density at ortho and para positions.
Thus:

- Deactivating overall
- Ortho–para directing

Quick Tip

Halogens are deactivating but ortho–para directing due to resonance.

(iv) Write the major product in the following reactions:
(1) Chlorobenzene + Na/dry ether

Solution:

This is Fittig reaction (coupling of aryl halides).

$$2C_6H_5Cl + 2Na \rightarrow C_6H_5{-}C_6H_5 + 2NaCl$$

Product: **Biphenyl**

Quick Tip

Aryl halide + Na (dry ether) → Fittig reaction → biaryl formation (e.g., biphenyl).

(2) p-Nitrotoluene with Br_2 (heat)

Solution:
Bromination in presence of heat leads to side-chain bromination.

$$p\text{-Nitrotoluene} \xrightarrow{Br_2,\ heat} p\text{-Nitrobenzyl bromide}$$

Quick Tip

$\mathrm{Br_2}$ + heat → side chain bromination (free radical substitution).